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Inorganic Compound Identification of Fly Ash Emissions from Municipal Incinerators

Battelle Columbus Labs., OH

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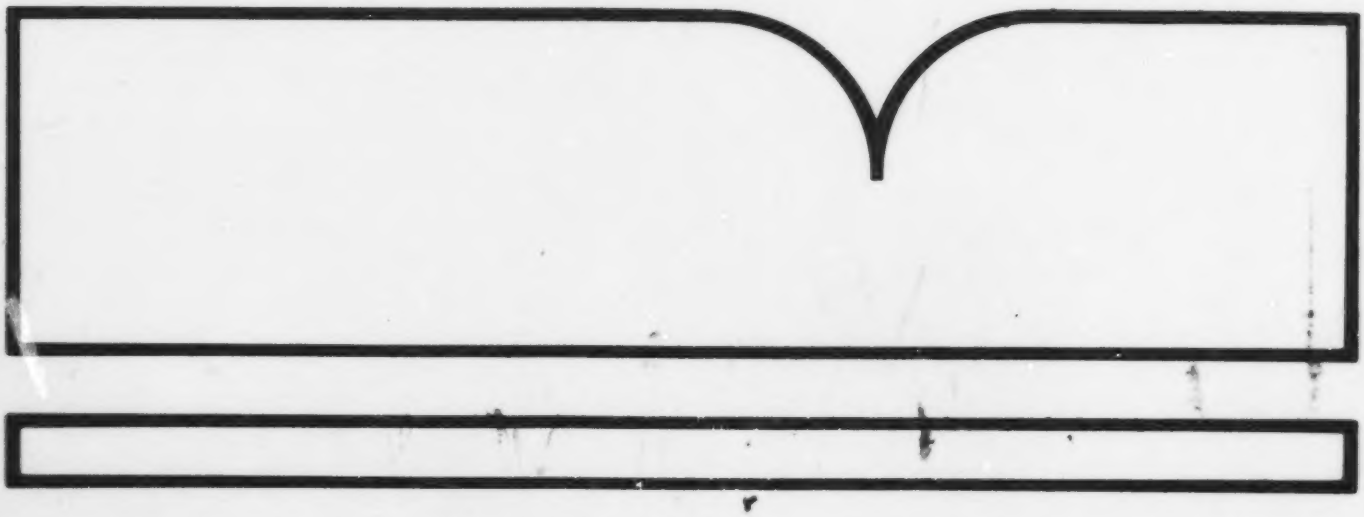

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INORGANIC COMPOUND IDENTIFICATION OF FLY ASH EMISSIONS FROM MUNICIPAL INCINERATORS

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ABSTRACT

Particulate matter emitted as fly ash from municipal refuse and sludge incineration operations consists largely (>90 percent) of inorganic species, including soot. Although commonly these inorganics are referred to as oxides, it is evident from the compositions of the wastes being combusted that chlorides, sulfates, and, in the case of sludge, phosphates are potential reactant products in the combustion process. This report presents a brief summary of existing data on the composition of ashes resulting from various municipal refuse and sludge incineration operations and new data as to the inorganic compounds present. Several samples of stack emission fly ash were collected and analyzed in detail for their elemental contents in order to provide insight as to the potential inorganic compounds possibly present. Then compound identification work was performed by X-ray diffraction (XRD) and Fourier Transform infrared (FT-IR) techniques. The compound analyses showed the presence of many inorganic compounds in addition to oxides in the fly ashes. The use of the FT-IR technique is detailed in the report because its application to inorganic species identification is relatively new.

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CONTENTS

Abstract iii

List of Figures vi

List of Tables vii

1. Introduction 1

2. Conclusions 3

3. Background 4

Municipal Refuse Ash 4
Sludge Refuse 5

4. Compositional Analysis 7

Test Samples 7
Compositional Analyses 7

5. Compound Identification 11

X-Ray Diffraction Analyses 11
FT-IR Analyses 11

6. Summary and Discussion of Compound Identification 25

Bibliography 28

LIST OF FIGURES

Number		Page
1	Water solubles, unbaked	14
2	Water solubles, baked	15
3	2nd derivative spectra of water solubles, baked. The particular sulfate cations associated with each band are noted	16
4	Subtraction of sample IV water solubles unbaked, minus baked	18
5	Water insolubles, unbaked	19
6	Water insolubles, baked	20
7	2nd derivative spectra of water insolubles, baked	22
8	2nd derivative spectra of water insolubles, baked	23

LIST OF TABLES

Number		Page
1	Estimated Annual Average American Refuse Composition	4
2	Range of Concentrations Found in Various Municipal Sludges . . .	6
3	Refuse and Sewage Sludge Incineration Fly Ash Study	8
4	Composition of Municipal Refuse and Municipal Sludge Incinerator Fly Ash Samples	9
5	Composition of Water Soluble Fractions	10
6	XRD Analysis of Refuse and Sludge Fly Ashes	12
7	Identifications Made on Incinerator Fly Ash Samples by IR and XRD	26

SECTION 1

INTRODUCTION

Particulate matter emitted to the atmosphere is of environmental concern because of the increasingly large tonnages involved. Municipal incinerators disposed of over ten percent of the some 200 million tons of household, institutional, and commercial solid wastes generated in the United States in 1972.[1] In 1976, thirty-five percent of the over 9 million tons of sewage sludge generated annually was incinerated.[2] Over the past few years disposal by incineration has lost some favor by municipalities due to concern over inability to meet pending air pollution standards as well as the higher operational costs and technical skills required as compared to landfill disposal. However this should change due to the magnitude of disposal tonnages involved together with the decreasing availability of landfill sites, plus the attraction of recovering energy through waste combustion. Thus, all facets of the environmental consequences of incineration emissions need to be addressed, including identification of the chemical nature of the particulate species being emitted from incineration operations. These fly ashes are principally inorganic in nature.

Methods for inorganic speciation of emission particulate matter are limited and those that are applicable are time-consuming and technical difficult to use. As a consequence inorganic constituents present in waste incineration emissions usually are determined only on the basis of their metal contents. Frequently these determined metal values are mathematically converted to oxides in order to show an approximate material balance for the fly ash composition; e.g., Si to SiO_2, Al to Al_2O_3, etc. Such arbitrary conversions can be misleading since the incineration fly ash can have a mixture of origins, including:

(1) Mineral residues not destroyed by the brief passage through the flame zone, or which bypass the central flame zone.

(2) Molten or solid material formed by condensation of elementary species in the immediate post-flame zone.

(3) Nucleated material from supersaturated vapors in the subsequent cooling zones.

(4) Material added to the existing particulate by physical and/or chemical absorption.

(5) Compositions formed by reactions of species in (1) through (4) above.

(6) Physical reconstitution, e.g., crystallization.

Note that in origin (2) the material undergoes rapid temperature change on the order of 2000 F in a few seconds, and therefore a considerable deviation from the equilibrium composition expected thermodynamically is expected. Based on these parameters it appears that incineration process fly ashes will consist of a complex mixture of amorphous and crystalline substances.

Inorganic speciation, what little has been done, has relied mostly on X-ray diffraction, morphological characterization of particle groups by microscopy, and indirectly, by scanning electron transmission and electron microprobe spectroscopy. X-ray diffraction is applicable only to crystalline compounds and, as in the case of fossil fuel combustion fly ash, incineration of waste would be expected to result in high concentrations of glassy amorphous species. Petrographic and other microscopic techniques can look at only small area and surfaces of samples and those are not representative of the total sample. Because of those limitations the use of Fourier Transform infrared (FT-IR) spectroscopy was emphasized in this program to identify inorganic species in fly ash emissions from waste incinceration operations.

The primary objective of this research program is to identify the inorganic compounds present in fly ash emissions from municipal refuse and sludge incineration operations. Due to the high combustion temperatures used these inorganic constituents should represent the major portion (> 90 weight percent) of these emissions. Since the application of FT-IR to inorganic compound identification and analysis is relatively new, its use on this program entailed considerable development efforts, including the preparation of additional spectra to our spectral reference library. These FT-IR development efforts limited the number of samples to which the compound analysis efforts could be applied, principally to two municipal refuse and one municipal sludge incinerator fly ash samples. These samples were judged representative of the waste incinceration fly ashes on the basis of their elemental contents.

A secondary objective of the program is to obtain data on the elemental (cation/anion) contents of fly ashes emitted from waste incineration operations. Most data given in the literature are on bottom ash and precipitator ash contents and not on ashes emitted to the atmosphere. Six incinerator operations were sampled and analyzed in detail to provide these data.

SECTION 2

CONCLUSIONS

Based on the samples of fly ash collected as particulate matter emitted from the stacks of municipal refuse and municipal sludge incinerators, elemental analyses of these and studies of their compound structures, the following conclusions have been reached:

(1) The particulate emissions from the incinerators are largely (>90 percent) inorganic in nature.

(2) The particulate emissions are from one-third to one-half water soluble.

(3) The water soluble phase of the municipal refuse incinerator fly ashes are principally chloride and sulfate salts of Na, K, Ca, Zn, and to a lesser extent, NH_4^+ salts.

(4) The water soluble phase of the municipal sludge incinerator fly ashes are principally sulfate, and to a lesser extent phosphate and chloride salts of Na, K, Ca, Zn, and NH_4^+.

(5) The water insoluble phase of the municipal refuse incinerator fly ashes are principally oxide and silicate salts of Al, Si, Ca, Pb, Zn and Fe, plus some insoluble sulfate salts and carbon products.

(6) The water insoluble phase of the municipal sludge incinerator fly ashes are principally oxide, silicate and phosphate salts of Al, Si, Ca, Pb, Zn and Fe plus insoluble carbon products.

(7) The major differences between the composition of the fly ashes from the two types of incineration processes are the high concentrations of chlorides, derived from plastics in the municipal refuse feed, and the high concentration of phosphates, derived from human and animal wastes, in the municipal sludge feed.

(8) In respect to compound identification, the Fourier Transform infrared technique provided more definitive information than was obtained by X-ray diffraction. Based on the comparatively low intensities of the X-ray patterns, both types of incinerator fly ashes appear to be highly amorphous in nature and, as such, not as amenable to XRD as to FT-IR analysis.

SECTION 3

BACKGROUND

Little data have been reported in the open literature on the compositions of particulate matter emitted as fly ash from municipal refuse and sludge incineration operations. Fairly complete elemental analyses have been reported on bottom ash and precipitator and scrubber-contained ashes since these represent considerable bulk and must be disposed of, usually in landfills where they are subject to leaching action. However, even these compositional data often have not included the anion contents of the samples.

MUNICIPAL REFUSE ASH

Potential pollutants in municipal refuse incinerator feed vary widely dependent on local industrial activities, refuse collection and disposal regulations, and incinerator operation practices. The average gross composition of refuse from 23 U.S. cities given by Corey[1] is shown in Table 1. Kaiser[3] found that the sulfur content of municipal refuse is relatively low, being 0.1 to 0.15 percent, and concluded that during combustion only a minor fraction of the sulfur is released as SO_2 while a major fraction is fixed in the ash which has alkaline oxides. Other investigators have found up to 0.3 percent sulfur in refuse. Carotti and Kaiser[4] determined the concentrations of 20 gaseous chemical species in the flue gas of a municipal incinerator and concluded that HCl acid is a major constituent of these gaseous emissions. Jahnke, et al[5] also performed a study of gaseous emissions from a municipal incinerator and found that emission levels could be correlated to the combustion conditions existing within the incinerator. Greenberg, et al[6] analyzed multiple samples

TABLE 1. ESTIMATED ANNUAL AVERAGE AMERICAN REFUSE COMPOSITION[1]

Component	Mean Weight, %	Description
Glass	9.9	Bottles mainly
Metal	10.2	Cans, wire, foil
Paper	51.6	Various types, some with fillers
Plastics	1.4	PVC, polyethylene, styrene, etc.
Leather and rubber	1.9	Shoes, tires, toys, etc.
Textiles	2.7	Cellulosic, protein, and woven synthetics
Wood	3.0	Packaging, furniture
Food wastes	19.3	Garbage
Total	100.0	

of fly ash collected from the municipal incinerators in the Washington, D.C. area and concluded that, while refuse incineration contributes only a few percent of the TSP of most cities, the particles are so rich in trace elements that incinerators are major sources of airborne Cd, Zn, Sb, and possibly Sn, Ag, and In. In a journal article Freeman[7] cites an NSF study which found that, in two metropolitan areas, refuse incineration could account for major portions of Zn, Cd, and Sb observed in airborne particles and the study also suggested that incineration was a large source of vapor phase mercury. Eiceman, et al[8], working with grab and electrostatic precipitation samples from municipal refuse incinerators, obtained detailed analyses of about 100 trace organic compounds in "fly ash" samples collected from municipal incinerators in Japan, Canada, and The Netherlands. Total organic mass extracted with benzene was 1 to 30 μg/g. Of importance was their finding that the sum of tetrachlorodibenzo-p-dioxin isomers was 2 to 10 μg/g. An EPA study[9] of atmospheric emissions of HCl emissions from two municipal refuse energy recovery systems established both emission factors and mass emission rates. The projected ambient HCl levels raise a question of significant materials damage resulting from uncontrolled emissions.

SLUDGE REFUSE

As with municipal refuse, the composition of municipal sludge varies with the locality from which it is derived. Furr, et al[10] made extensive analyses of the sludge contents of 16 American cities sampled during 1972 and 1973 and found the range of concentrations shown in Table 2. On incineration, of course, many of the elements shown in Table 2 are enriched in the ash products of combustion and in the gaseous vapors emitted from stacks. Note the high concentration of phosphorus in the sludge, possibly derived from human wastes and/or industrial detergents. Gabler[11] and his coworkers determined the concentration of the major and trace metals in ashes, presumably taken from bottom or control device matter, and, in a study of leaching, found that most elements of environmental concern could be removed by a single stage acid leach. Furr and Parkinson[12] made an analytical survey of 42 elements and polychlorinated biphenyls (PCB's) in municipal sewage sludge ash from 10 U.S. cities. Again, these were bottom and scrubber ash products. PCB's were not detected in these samples. While the contents of Ni and Zn were found to be quite high in the ashes, the absorption of these in cabbage grown in ash-amended soil was low, possibly due to their presence as insoluble products. Elements such as Cd, Hg, Ni, and Se were low in the ashes studied, probably due to volatilization losses during incineration. Greenberg, Zoller, and Gordon[13] determined the metal contents of 36 metals in fly ash emitted from a well-controlled fluidized bed sewage sludge incinerator. They found the stack emissions of trace elements in particles to be quite small in this type of incineration process and assumed that most of the elements analyzed were contained in the scrubber water. Shilesky and Wyatt[14] state that the ash generated from the combustion of sludge may be a potential pollutant source when placed in a landfill which could produce leachate and find this ash to be moderately basic with water solubility under about two percent. This solubility value is very low, possibly indicating low sulfate, chloride, and phosphate concentrations in bottom ashes.

TABLE 2. RANGE OF CONCENTRATIONS FOUND IN VARIOUS MUNICIPAL SLUDGES[10]
Dry Weight Basis
Parts per Million, Except Where Indicated

Element	Range	Element	Range
Ash	30.9 - 59.4%	Cu	458 - 2890
Ca	0.86 - 11.64%	Ge	1.3 - 10.5
Cl	0.05 - 1.02%	Hg	3.4 - 18
Fe	0.88 - 8.28%	In	0.07 - 3.7
K	0.27 - 3.87%	Ir	0.03 - 0.46
Mg	0.2 - 1.13%	Mn	32 - 350
N	1.48 - 5.80%	Mo	1.2 - 40
Na	0.08 - 1.19%	Ni	36 - 562
P	0.96 - 2.72%	Pb	136 - 7627
As	3 - 29	Pt	0.05 - 0.64
Au	0.21 - 7.0	Sb	2.6 - 44.4
Ba	272 - 1066	Se	1.7 - 8.6
Bi	0.03 - 55.8	Sn	111 - 492
Cd	6.8 - 443	Ti	1080 - 4580
Co	3.7 - 1066	V	14.8 - 91.5
Cr	169 - 14,000	Zn	560 - 6890
Al	0.81 - 5.12%	Dieldrin	0.03 - 2.2
		PCB	0,01 - 23,1

SECTION 4

COMPOSITIONAL ANALYSIS

TEST SAMPLES

Fly ash samples were collected from the stack sampling ports (beyond any control device) of municipal refuse and municipal sludge incinerator plants. Also a fly ash sample was collected from the stack port of an in-house pilot-scale stoker-boiler in which dry pelletized municipal refuse was combusted. A description of the sampling sources is given in Table 3.

COMPOSITIONAL ANALYSES

The samples were analyzed for their cation/anion contents, shown in Table 4. Trace metal contents were determined by spark source mass spectrometry (SSMS), higher concentrations of metals were determined by inductively-coupled plasma optical emission spectrometry (ICAP), by atomic absorption spectrometry (AAS), and by X-ray fluorescence (XRF). Anions were determined by ion chromatography, specific ion electrodes, and colorimetric procedures.

As seen in the tabular data and as would be expected from the high temperature combustion processes, the particulate emissions consist principally of inorganic matter including relatively high concentrations of carbon, presumably uncombusted soot. The $MeCl_2$ solubility data indicate an approximate total organic fraction of 3 to 7 percent. The analyses show the fly ash emissions to be from 34 to 47 percent water soluble and weakly acidic in the water extraction solution. The refuse ashes are characterized by high concentrations of $SO_4^{=}$, Cl^{-}, and low $PO_4^{\equiv}$, and NO_3^{-} contents while the sludge-derived incinerator fly ashes contain high $SO_4^{=}$ and $PO_4^{\equiv}$ but low Cl^{-} anions. The NO_3^{-} and NH_4^{+} contents of the sludge fly ashes are higher than those found in the municipal refuse fly ashes as are many of the heavy metals, especially Cr, Ni, Cu, Ag, Cd, Sn, Pb, and Bi. There are little differences between the municipal refuse and municipal sludge fly ash types in respect to the concentrations of the major alkali, alkaline earth and silicon components. The total oxygen contents of the samples were not determined.

The water soluble fractions of the fly ash samples, comprising one-third to nearly one-half of the total samples collected, were analyzed for their cation/anion contents giving results shown in Table 5. These results indicate the municipal refuse water soluble fly ashes to be principally Na, Zn, K, and Ca, chloride and sulfate salts, or combined salts of these. The water-soluble sludge fly ashes appear to be principally Zn, NH_4^{+}, Na, K, and Ca, sulfate, phosphate, and chloride salts or complexes thereof.

TABLE 3. REFUSE AND SEWAGE SLUDGE INCINERATION FLY ASH STUDY

	Refuse			Sludge		
BCL Code Site	I	II	III	IV	V	VI
Incinerator type	Water wall boiler recip. mech. stoker	Water wall boiler with stoker	Water wall stoker-boiler	Multiple hearth 7-stage	Refractory wall	Multiple hearth 5-stage
Start-up year	1972	1979	1978	1974	1970(?)	1974(?)
Fuel, if used	Fuel oil #2	Fuel oil #2	Coal start	Gas for start	Natural gas	Fuel oil #2 and reconditioned oil
Heat recovery	Building heating	Steam sold	No	Some for Zimpro	No	No
Refuse or sewage feed rate	30 tons/hr or refuse	20 tons/hr of refuse	60-100 lb/hr of refuse	7 tons/hr of vacuum filtered Zimpro processed sludge and pulp	10 tons/hr vacuum filtered primary and secondary sludge	10 tons/hr vacuum filter primary and secondary
Emission control	ESP	ESP	None	Venturi scrubber	Venturi scrubber	Venturi scrubber
Sample system	Vacuum canister	Vacuum canister	SASS train and Method 5	Vacuum canister	Method 5	Method 5
Sample mass	65 g	7.5 g	16 g	16.5 g	167 mg	257 mg

TABLE 4. COMPOSITION OF MUNICIPAL REFUSE AND MUNICIPAL SLUDGE INCINERATOR FLY ASH SAMPLES (Results in Percent)

Determination	Municipal Refuse			Municipal Sludge		
	I	II	III	IV	V	VI
pH[(a)]	5.8	6.0	5.5	5.1	5.3	5.2
Water soluble[(b)]	37.1	47.4	42.1	34.1	43.3	43.0
$MeCl_2$ Soluble	6.8	3.4	3.2	3.1	7.3	3.9
Total C	9.5	13.2	20.6	17.8	10.8	5.1
Total H	0.5	1.1	0.7	1.1	1.7	3.3
NO_3^-	0.03	0.25	0.04	0.36	0.40	0.22
NH_4^+	0.09	0.90	0.45	1.71	1.80	1.95
$SO_4^=$	13.0	16.3	9.25	16.9	9.45	10.0
$PO_4^=$	2.0	1.2	0.5	12.2	12.5	9.9
Cl^-	10.0	17.0	15.4	2.7	1.8	1.0
Na	4.8	11.0	8.5	3.0	2.8	3.3
Mg	1.5	1.9	1.1	0.9	0.20	0.40
Al	6.0	2.0	4.1	2.0	3.2	3.0
Si	7.5	5.0	5.4	5.1	11.1	13.5
K	5.1	7.2	6.0	6.0	2.8	2.5
Ca	5.9	3.0	5.0	7.1	6.0	6.0
Ti	1.9	0.5	0.5	0.4	0.2	0.10
V	0.01	<0.01	<0.01	0.02	0.02	0.04
Cr	0.12	0.09	0.04	0.80	0.60	0.30
Mn	0.18	0.06	0.05	0.14	0.04	0.04
Fe	3.9	1.1	3.3	3.6	4.0	4.4
Ni	0.09	0.01	0.01	0.05	0.15	0.06
Cu	0.20	0.21	0.15	0.55	0.30	0.50
Zn	6.4	4.3	8.0	5.0	12.0	10.2
As	0.06	0.04	0.10	0.06	0.02	0.04
Ag	0.03	0.03	0.01	0.10	0.03	0.05
Cd	0.11	0.13	0.10	0.40	0.25	0.30
Sn	0.8	0.66	0.5	1.2	0.45	0.40
Sb	0.20	0.23	0.8	0.04	0.10	0.10
Ba	0.08	0.07	0.05	0.12	0.06	0.07
Pb	2.6	3.5	4.9	3.5	3.2	3.3
Bi	0.05	0.03	0.01	0.20	0.07	0.20

(a) pH determined on the water-soluble extract
(b) Water-soluble determined by stirring 1 g of sample in 75 ml water at room temperature for one hour.

TABLE 5. COMPOSITION OF WATER SOLUBLE FRACTIONS

Sample	Municipal Refuse Fly Ashes			Sewage Sludge Fly Ashes		
	I	II	III	IV	V	VI
C*						
H*						
NO_3	0.08	0.53	0.1	1.05	0.92	0.51
NH_4	0.24	1.9	1.1	5.0	4.15	4.5
$SO_4^{=}$	30.6	28.5	17.3	46.3	20.7	22.3
PO_4	0.03	0.02	0.07	2.9	5.3	5.35
Cl^-	28.3	27.4	36.0	7.0	4.15	2.3
Na	10.3	19.0	12.4	3.0	4.4	6.5
Mg	0.6	0.2	0.4	0.75	0.35	0.7
Al	<0.01	<0.01	0.02	<0.01	0.5	0.4
Si	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
K	9.5	11.2	10.3	4.1	4.4	3.5
Ca	5.7	2.3	2.2	7.4	6.2	5.6
Ti	<0.03	<0.03	<0.03	<0.03	0.11	<0.01
Cr	<0.01	0.04	0.07	1.75	0.25	0.51
Mn	0.10	0.02	0.02	0.15	0.18	0.05
Fe	0.25	0.2	<0.01	<0.15	0.05	2.3
Ni	0.14	<0.01	0.02	0.05	0.18	0.07
Cu	0.08	<0.01	0.3	1.2	0.45	0.45
Zn	9.2	3.2	10.6	7.9	16.88	18.6
As	0.08	0.04	0.12	0.09	0.02	0.02
Ag	0.05	0.02	0.01	0.1	0.05	0.02
Cd	0.25	0.19	0.16	0.9	0.35	0.6
Sn	<0.01	<0.01	<0.01	<0.01	0.07	0.23
Sb	<0.01	<0.01	<0.01	0.02	<0.01	<0.01
Ba	0.02	<0.01	0.02	0.03	<0.01	0.02
Pb	0.05	0.02	0.7	<0.01	0.9	1.6
Bi	0.02	<0.01	<0.01	0.15	<0.01	0.05

*Not applicable

SECTION 5

COMPOUND IDENTIFICATION

Prior work on coal- and oil-fired power plant fly ash emissions[15,16] has shown that it is advantageous to analyze the water insoluble and water soluble phases of the samples as well as the total unseparated sample in seeking the compounds present. The insoluble phase should contain the oxides and glass phases of the samples as well as insoluble sulfate and phosphate forms while the water soluble phases should contain the soluble sulfate, chloride, nitrate, and any soluble phosphate forms contained in the total samples. Identification of compounds in the separated phases aids in the interpretation of the XRD patterns and FT-IR spectra found in the total samples.

X-RAY DIFFRACTION ANALYSES

Two municipal refuse and one municipal sludge fly ash samples were analyzed by X-ray diffraction using CuK_2 excitation and strip chart recording over a 2 θ range from 15 to 70 degrees.

The X-ray diffraction pattern intensities obtained were relatively weak, possibly attributable to a low concentration of crystalline substances in the samples. The qualitative identifications made are given in Table 6. In each sample, compounds were identified in the water-insoluble phase which could not be identified in the total sample. The identification of K_2ZnCl_4 was noteworthy. There is little in the literature on this compound so a reference was prepared to confirm the pattern and, although the reference was prepared from a solution rather than a gas phase state, this identification appears to be reasonably certain.

FT-IR ANALYSES

The same group of samples was analyzed by FT-IR using techniques previously developed for fossil fuel power plant particulate emissions.[17,18] Infrared spectra were obtained on the H_2O soluble and H_2O insoluble fractions of the samples both before (unbaked) and after heating at 200 C (baked to remove waters of crystallization and to remove readily volatile components). Our computerized spectral search program was used for the water soluble fraction spectra. This search program presently is only of substantial use on sulfate species (mainly on the H_2O soluble fraction in which the sulfates predominate) since our reference spectra library is primarily composed of sulfate salts. A new technique, that of obtaining second derivative spectra, was used to assist in the data interpretation. The second derivative spectra are useful in resolving a complex peak into its components. This overcomes a major problem in identifying

TABLE 6. XRD ANALYSIS OF REFUSE AND SLUDGE FLY ASHES

Sample	Compound	PDF #	Pattern Strength
I	Halite (NaCl)	5-628	100
As Received	Anhydrite ($CaSO_4$)	6-226	60
	Quartz (α-SiO_2)	5-490	20
	K_2ZnCl_4	30-1015	20
	$KAl(SO_4)_2$	3-337	20
	Unknown		25
I	Quartz (αSiO_2)	5-490	100
H_2O Insoluble	Anhydrite ($CaSO_4$)	6-226	60
	Anglesite ($PbSO_4$)	5-577	60
	Magnetite (Fe_3O_4)	19-629	40
	Hematite (α-Fe_2O_3)	13-534	30
	Halite (NaCl)	5-628	10
	Unknown		60
II	Halite (NaCl)	5-628	100
As Received	Quartz (α-SiO_2)	5-490	10
	Anhydrite ($CaSO_4$)	6-226	10
	K_2ZnCl_4	30-1015	10
	Unknown ($MeCl_2$ Soluble)		30
	Unknown ($MeCl_2$ Insoluble)		20
II	Quartz (α-SiO_2)	5-490	100
H_2O Insoluble	Calcite ($CaCO_3$)	5-586	30
	Anhydrite ($CaSO_4$)	6-226	20
	Magnetite (Fe_3O_4)	19-629	15
	Unknown		30
IV	Anhydrite ($CaSO_4$)	6-226	50
As Received	Quartz (α-SiO_2)	5-490	40
	Unknown ($MeCl_2$ Soluble)		100
	Unknown ($MeCl_2$ Insoluble)		70
IV	Quartz (α-SiO_2)	5-490	90
H_2O Insoluble	Unknown		100
V	Calcite ($CaCO_3$)	5-586	50
As Received	Goethite (α-FeOOH)	29-713	40
	$Fe_4(P_2O_7)_3$	24-526	70
	Quartz (α-SiO_2)	5-490	30
	Halite (NaCl)	5-628	30
	Calcite ($CaCO_3$)	5-586	30
	Unknown		20

specific compounds in a mixture of similar compounds by determining the exact frequencies of several overlapping bands. This use is illustrated in the following sections.

Water Soluble Fractions

The infrared spectra of the unbaked water soluble fractions of samples I, II, and IV are shown in Figure 1 while the corresponding baked fractions are shown in Figure 2. From the spectra of the unbaked water solubles (Figure 1), samples I and II appear to be quite similar, i.e., samples I and II show the same infrared bands differing only in the relative intensities of the bands. This means that samples I and II apparently differ only in the relative amounts of the individual components of the samples. From the bands near 1140 and in the 600-700 cm^{-1} region it is apparent that these two samples (unbaked water solubles) are primarily sulfates. Sample IV (Figure 1) shows spectral differences (3300 and 1400 cm^{-1} bands) from samples I and II, but is still mainly composed of sulfates (1140 cm^{-1} bands). In the spectrum of sample IV, the 3300 and 1400 cm^{-1} bands indicate the presence of ammonium ion.

From the bands at 600, 670, 1110, 3400, and 3550 cm^{-1}, it is immediately obvious that all three samples contain $CaSO_4 \cdot 2H_2O$ to a greater or lesser degree. Sample I contains the most $CaSO_4 \cdot 2H_2O$ and sample II contains the smallest amount of this component.

A comparison of the spectra of the baked water soluble samples to those of the unbaked water solubles shows two differences upon baking. This first difference is that the hydration bands (3550 and 3400 cm^{-1}) have disappeared upon baking as the $CaSO_4 \cdot 2H_2O$ is converted to $CaSO_4 \cdot 1/2\ H_2O$. This is one of the necessary identification changes in our inorganic speciation technique and definitely establishes the presence of $CaSO_4$ in all three samples.

The second difference between the spectra of the baked and unbaked samples is that the bands (in sample IV) due to the ammonium ion (3300 and 1400 cm^{-1}) are lost upon heating. Since most (if not all) ammonium sulfates are volatile upon heating, this helps to confirm the presence of ammonium ions in sample IV. In addition, the residual band at 1430 cm^{-1} in the baked spectrum of sample IV indicates the presence of a carbonate.

Using the computer search to match reference spectra to the sample spectra firmly establishes the presence of $CaSO_4$ in all three samples. The search system also indicated the probable presence of $ZnSO_4$ in sample I and the possible presence of $ZnSO_4$ in samples II and IV. In addition, the search demonstrated that Na_2SO_4 and K_2SO_4 were possibly present in these samples.

Even though the computer search indicated the possibility of several sulfates being present in each sample, the spectra of the sulfate bands (1150 cm^{-1} and the 600-700 cm^{-1}) of the three samples are similar. The sulfate bands of the various components overlap making positive identifications difficult. This overlap can be resolved by the use of 2nd derivative spectra. An example of this is shown in Figure 3 which gives the 2nd derivative spectra of the baked water soluble fractions of the three samples. The 2nd derivative spectra of samples I and IV are very similar and indicate the presence of at least 5

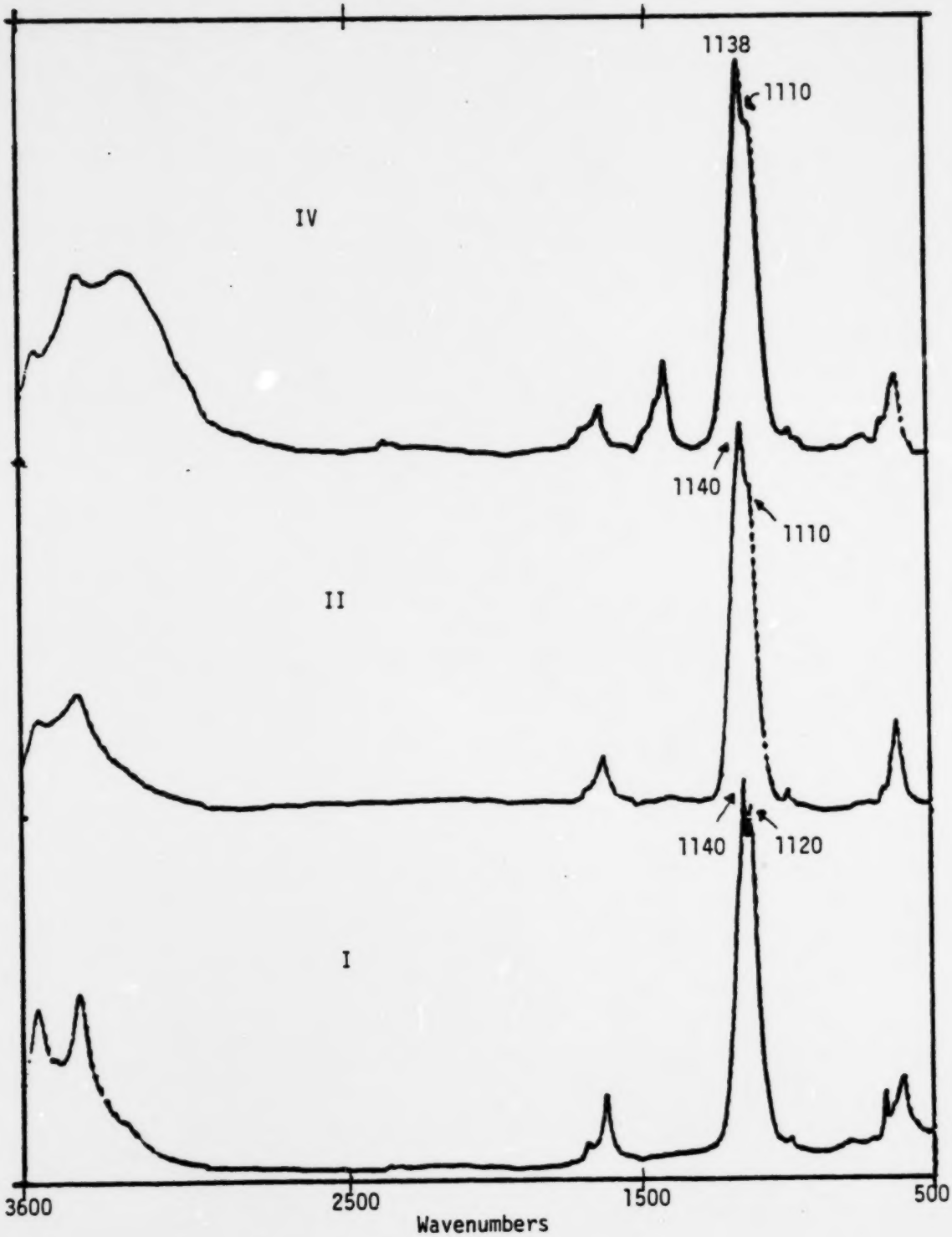

Figure 1. Water solubles, unbaked.

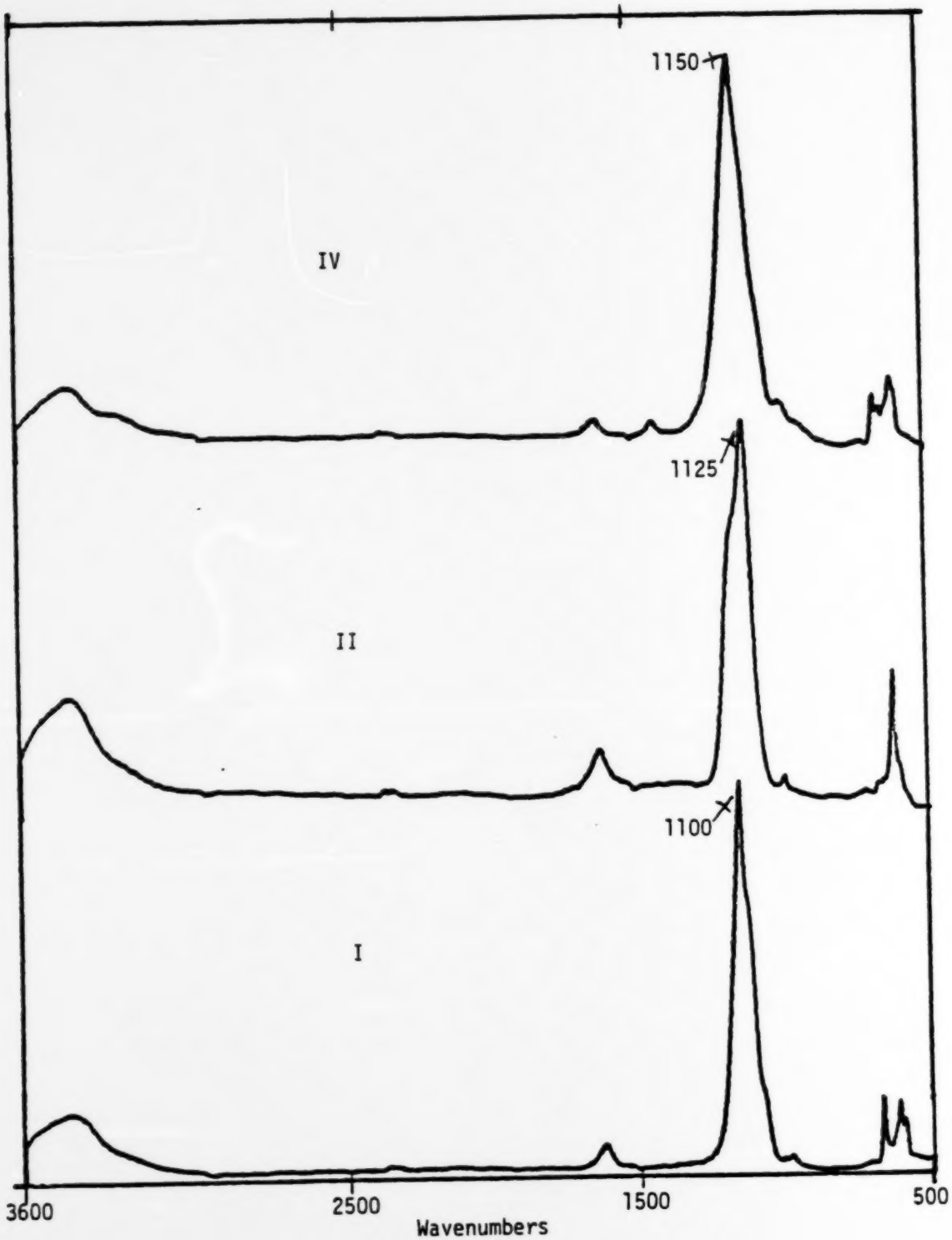

Figure 2. Water solubles, baked.

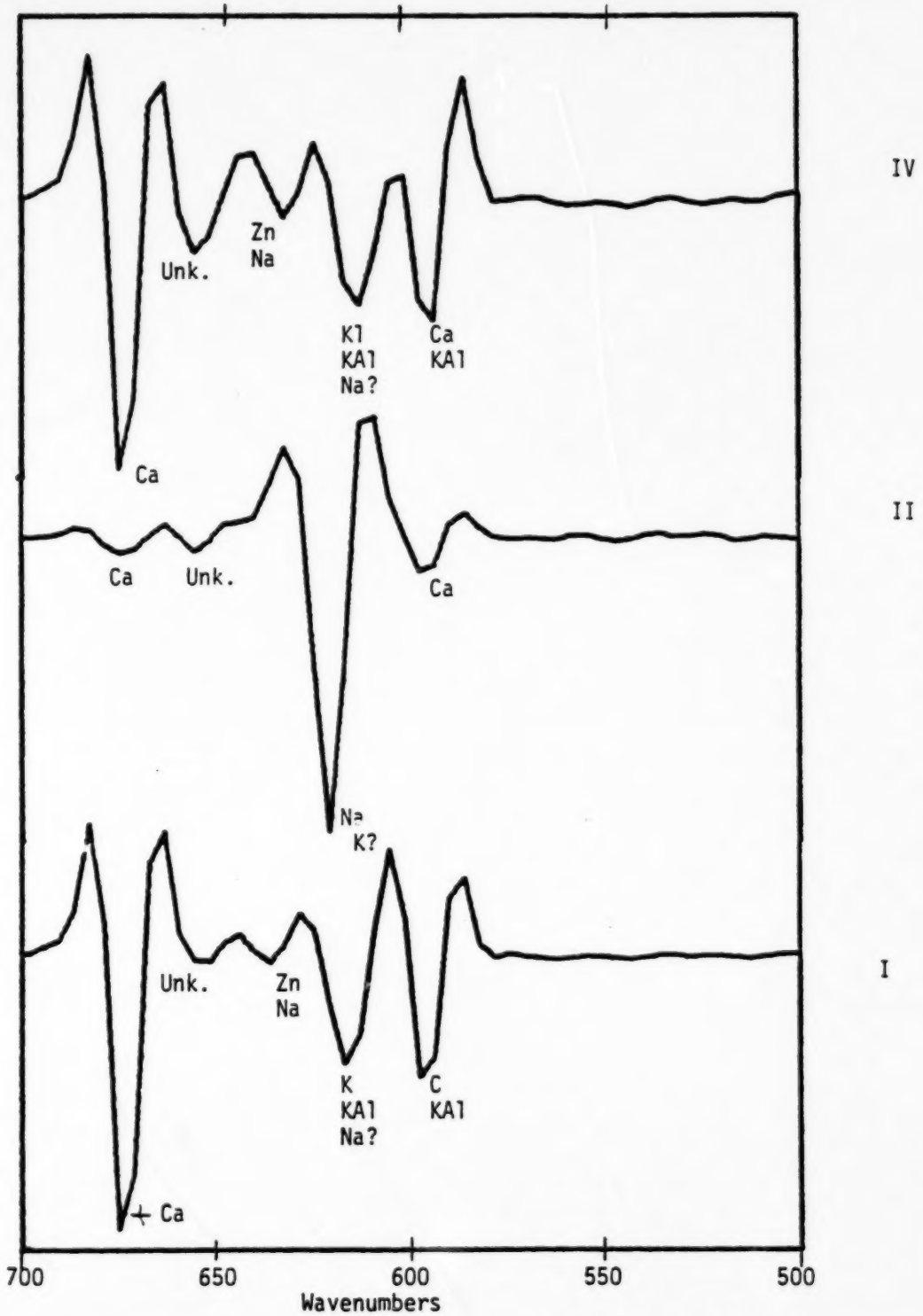

Figure 3. 2nd derivative spectra of water solubles, baked. The particular sulfate cations associated with each band are noted.

sulfate components. Remember that in sample IV, baking removed ammonium ion which is probably present as an ammonium-containing sulfate. Thus, after removal of ammonium, the sulfate composition of samples I and IV is almost identical. The probable assignments for these bands are listed on the spectra in Figure 3. Sample II contains some $CaSO_4$ but not nearly as much as in samples I and IV. Instead the 2nd derivative spectra indicate that Na_2SO_4 and possibly K_2SO_4 are the major sulfate components of sample II. From the infrared spectra of Figure 2 (baked water solubles), K_2SO_4 is probably present as a major component in sample II. Both samples I and IV contain an unidentified sulfate, while sample II contains smaller amounts of the unknown. Samples I and IV could also contain $KAl(SO_4)_2$.

It was previously stated that ammonium was removed upon heating sample IV and that this NH_4^+ was probably present as a sulfate. To identify the particulate sulfate, the spectrum of H_2O soluble baked, sample IV (Figure 2) was subtracted from a spectrum of H_2O soluble unbaked sample IV (Figure 1). The resultant subtraction is shown in Figure 4. The bands (pointing up in Figure 4 at 3300, 1400, 1100, and 620 cm^{-1}) match well with a reference spectrum of $(NH_4)_2SO_4$.

Water Insoluble Fractions

Spectra of the unbaked and baked water insoluble fractions of the three samples are shown in Figure 5 and 6, respectively. There was, as expected, very little change upon heating so these samples will be discussed in terms of the baked sample spectra of Figure 6. These spectra are dominated by the strong infrared absorption in the 1060-1110 cm^{-1} region. For water insoluble species, there are three classes of compounds that have major absorption bands in this region:

(1) Silicates, which are all H_2O insoluble,

(2) Phosphates, many of which are H_2O insoluble, and

(3) Sulfates, a few of which are H_2O insoluble.

Although small amounts of sulfates could be present, sulfates cannot be the major component giving rise to the 1060-1110 cm^{-1} infrared band because: (1) from past analyses of fly ash samples, very little sulfate has been detected in the water insoluble fractions; (2) most sulfates give an infrared band above 1100 cm^{-1}, not below 1100 cm^{-1}; and (3) there is not enough infrared absorption in the 600-700 cm^{-1} range to indicate large amounts of sulfates.

Except for sample IV (which will be discussed later), phosphate cannot be the major component of the 1060-1100 cm^{-1} absorption because: (1) the necessary confirming bands for P-O compounds were not detected in the 500-650 cm^{-1} region, and (2) the elemental analyses of I and II (see Tables 3 and 4) only indicate small (2.0 and 1.1 percent $PO_4^{=}$) amounts of phosphates in these samples.

This means that silicates (Si-O compounds) must be the major component giving rise to the 1060-1110 cm^{-1} infrared absorption and must be a substantial portion of the water insoluble fractions. Because Si-O bonds are strong infrared absorbers and metal-oxygen bands are weaker, it is difficult for us to

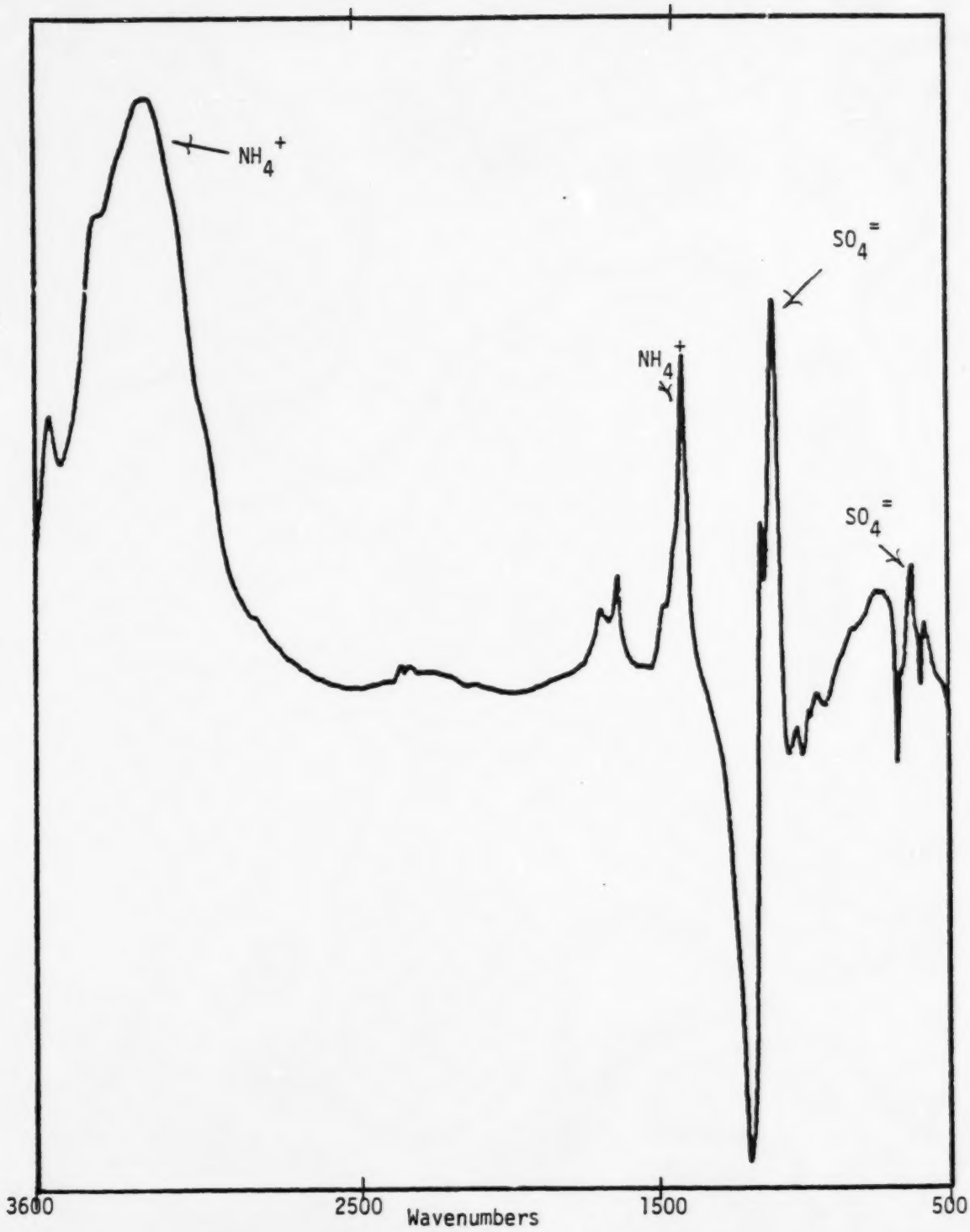

Figure 4. Subtraction of sample IV water solubles unbaked, minus baked.

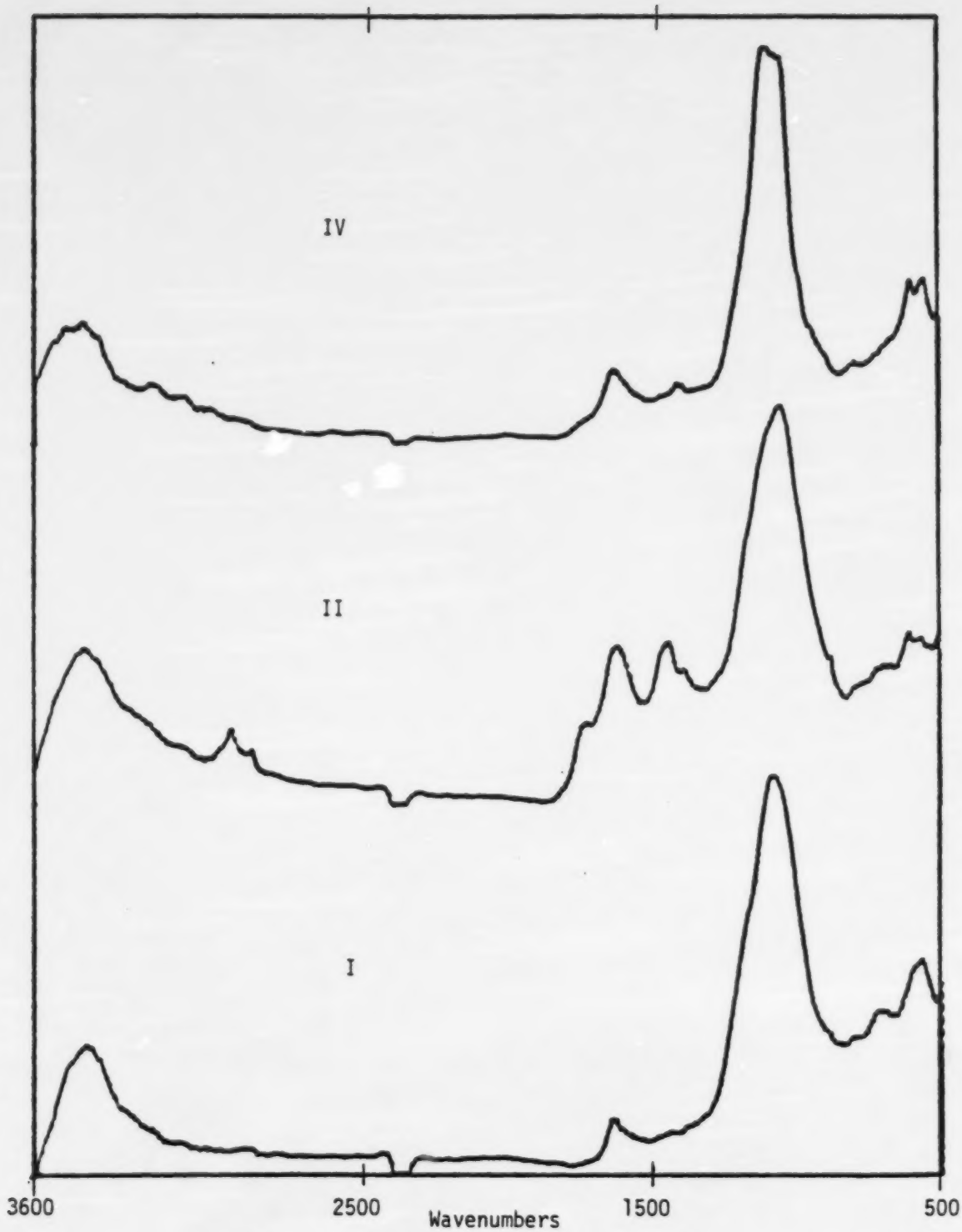

Figure 5. Water insolubles, unbaked.

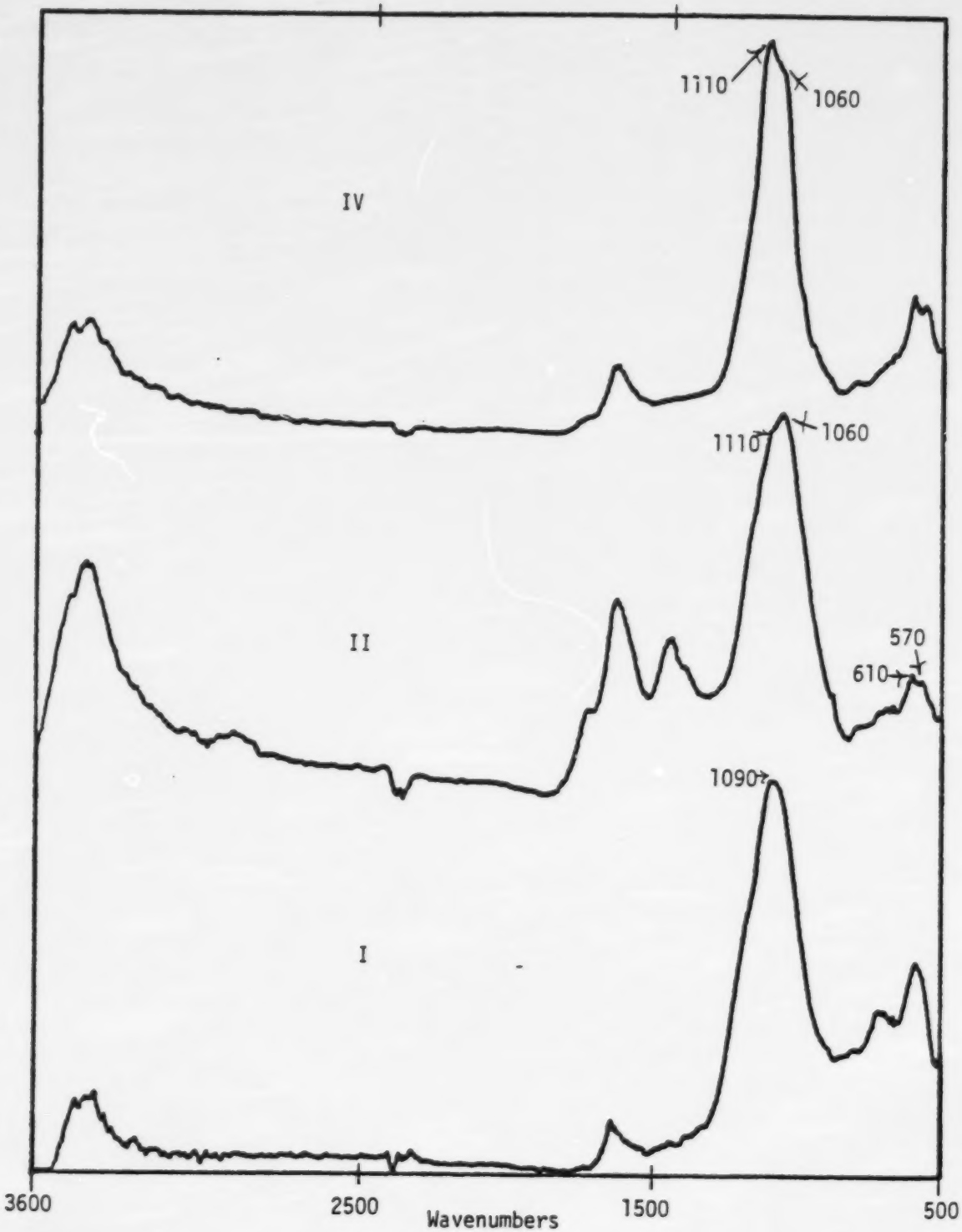

Figure 6. Water insolubles, baked.

ascertain if silicates or oxides are the major component of the H_2O insoluble fractions. The observation of a weak, complex band near 800 cm^{-1} incidates a small amount of quartz (α-Si-O_2) is present, but quartz does not account for the majority of the silicates (Si-O components).

Besides silicates, the spectra indicate that oxides are present in all three samples. Fe_3O_4 is observed in samples I and II (bands near 570 and 725 cm^{-1}) and Fe_2O_3 possibly appears in samples II and IV. Fe_2O_3 has bands at 560 and 450 cm^{-1}, but since the spectra cut off at 500 cm^{-1}, we did not observe the confirming 450 cm^{-1} infrared absorption. In addition, there is evidence for Al_2O_3 in samples I and II (IR bands at 630 and 585 cm^{-1} as well as broad underlying absorption between 700 and 550 cm^{-1}).

Besides silicates and oxides, the spectra of Figure 6 indicate the presence of $CO_3^{=}$ in sample II (band at 1435 cm^{-1}) and the intensity and frequency of the 1620 band indicates that the $CO_3^{=}$ is present as HCO_3^{-} rather than $CO_3^{=}$. No weak, sharp band in the 850 to 900 cm^{-1} region is observed which would help identify the cation associated with the HCO_3^{-} (bicarbonate). The second derivative spectra (in the 500 to 700 cm^{-1} region) shows bands near 600 and 630 cm^{-1} in sample II (but not in samples I or IV) which could indicate the presence of $PbSO_4$. These 2nd derivative spectra are shown in Figure 7. From this figure, it can be seen that sample IV shows bands near 553 and 617 cm^{-1} which are not seen in the 2nd derivative spectra of samples I and II. Since this is one region for P-O infrared absorption and since sample IV has a high (12.2%) $PO_4^{\equiv}$ concentration, it is likely that P-O is present in sample IV. Some substantiation of this can be seen in the 2nd derivative spectra of these samples in the 900 to 1200 cm^{-1} region (Figure 8). While there are many infrared bands in all of the spectra of Figure 8 (largely Si-O bands), it can be observed by comparing relative intensities that sample IV shows increased absorption at 1112, 1025, 1012, 998, 984, and 942 cm^{-1}. Many P-O compounds give bands near these frequencies and this combined with the observed bands in the 500 to 650 cm^{-1} region and the elemental analysis indicates a strong probability that P-O compounds are present in sample IV.

It is difficult to determine the exact nature of the P-O bonding since our reference spectra library of P-O compounds is small. From the combination of this reference spectra library and a small number of literature spectra, it appears that sample IV contains a mixture of phosphates ($PO_4^{\equiv}$) and dibasic phosphates ($HPO_4^{=}$) with the possibility of some pyrophosphate ($P_2O_7^{-4}$). The observed frequencies most nearly match (but do not exactly match) those of the various calcium P-O compounds.

Only the unbaked and baked (200 C for 3 hours) spectra of sample V was examined. The following results were obtained:

(1) V has more quartz (α-SiO_2) than samples I, II, or IV.

(2) V is probably low in $SO_4^{=}$ since the baked samples do not show $SO_4^{=}$ bands in the 600 to 700 cm^{-1} range. V very likely has some $SO_4^{=}$ or $PO_4^{\equiv}$ since there is a shift from 1090 cm^{-1} to 1110 cm^{-1} upon baking (the computer search indicates a possibility of NaH_2PO_4).

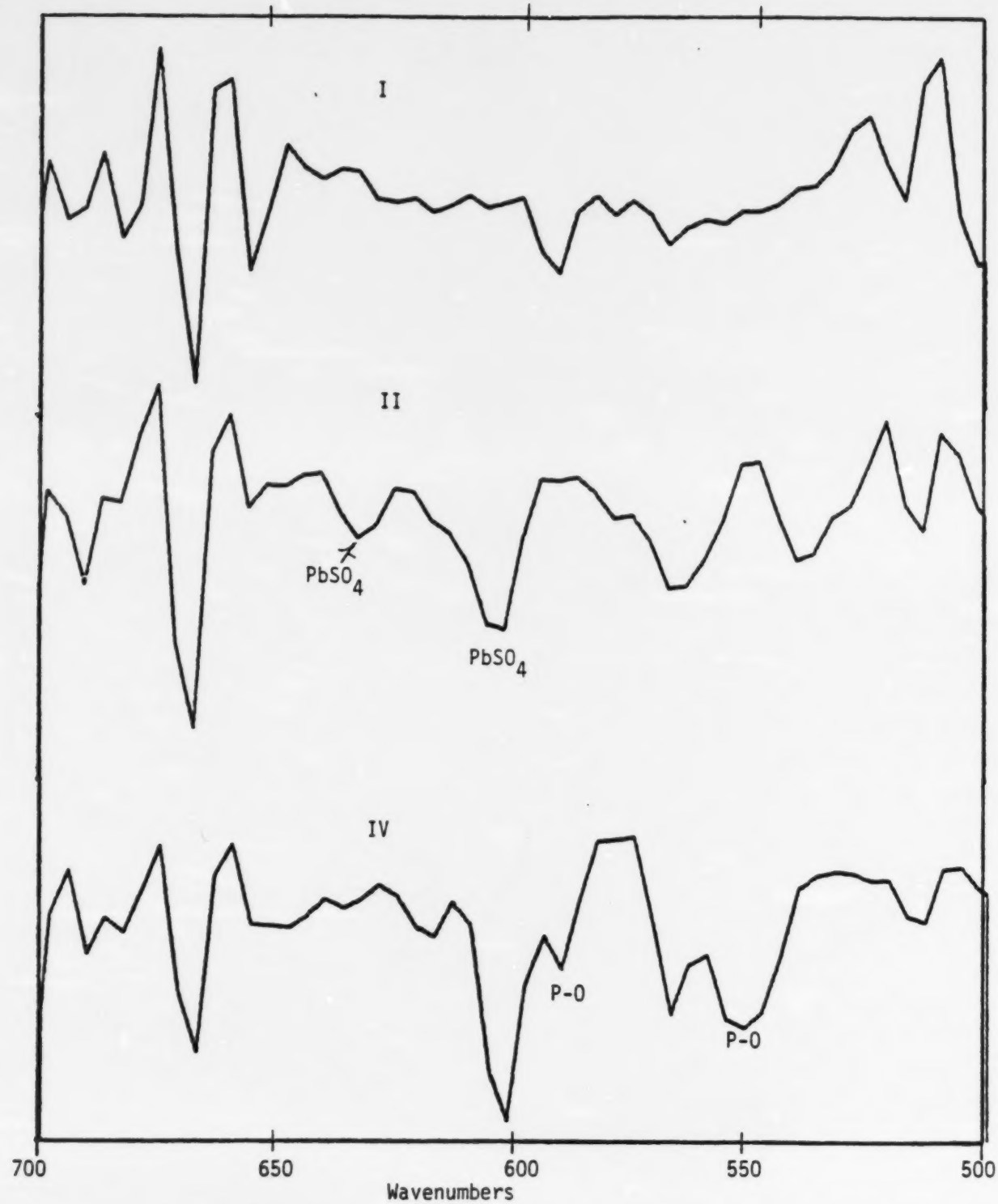

Figure 7. 2nd derivative spectra of water insolubles, baked.

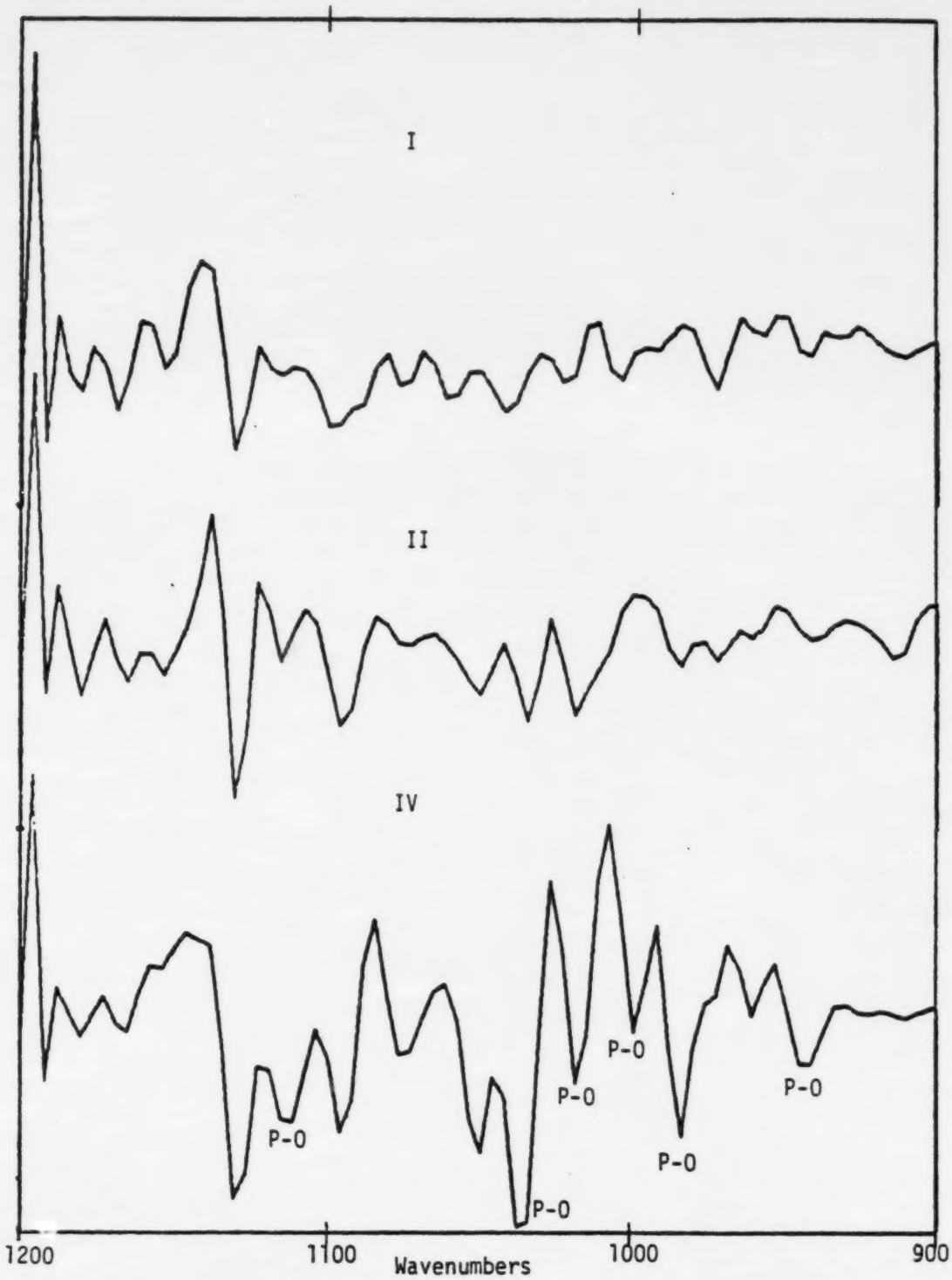

Figure 8. 2nd derivative spectra of water insolubles, baked.

(3) V does not appear to have any NH_4^+.

(4) V does have some $CO_3^=$.

(5) V likely has a similar oxide content to sample I, i.e., contains Fe_3O_2 and Al_2O_3.

Total Samples

In order to ascertain whether or not components of the sample had been lost during the separation procedure, the spectra of all the fractions were compared to the spectra of the total sample (before extraction). All infrared bands seen in the spectra of the total samples were also seen in the spectra of one of the fractions of that sample. This indicates that if components were lost during the separation procedure they were the same as the species identified in the spectra of the fractions, i.e., no species were lost preferentially. Thus, there does not appear to be any unobserved or unidentified compound and the analyses of the fractions represents the true composition of the samples.

SECTION 6

SUMMARY AND DISCUSSION OF COMPOUND IDENTIFICATION

Although IR and XRD data are not in complete agreement, correlations between the two sets of data fit relatively well (see Table 7) in which the data from the total, water soluble and water insoluble analyses have been combined. In general, the IR technique gives more total information due to the IR capability to provide analyses and speciation of the water soluble components, the amorphous components and organics. The latter capability was not utilized on this program. The incineration fly ash samples appear to be not highly crystalline. This does not adversely affect obtaining IR spectra but of course, does limit identification by XRD. XRD, on the other hand, provides information on inorganic chlorides (which give no IR bands) and identifies oxides with more certainty.

From the IR data alone it is relatively easy to distinguish between types of incineration emission sources (i.e., between refuse and sewage sludge fly ash samples). For example, the sewage sludge fly ash samples contain inorganic P-O compounds and $(NH_4)_2SO_4$ which are found only in very low amounts in the refuse fly ashes.

Both fly ash types contain high quantities (34 to nearly 50 percent) of water soluble components, mostly sulfate, chloride and, in the case of sludge fly ashes, phosphate salts. These emissions obviously pose more of an environmental problem than would be encountered if they were of a more chemically inert nature such as glassy or oxide structures.

The FT-IR technique has been shown in this work and in prior related studies (15-19) to be useful for the identification of inorganic species in environmental samples. With a more complete spectral reference library, sulfate, nitrate, oxide and other metal and ammonium salts can be individually identified in samples, in most cases, more completely than can be done using XRD. In areas where inorganic compound identification is of concern, such as acid deposition studies, the FT-IR technique should be considered for use at least as a complement to XRD and other compound identification techniques.

TABLE 7. IDENTIFICATIONS MADE ON INCINERATOR FLY ASH SAMPLES BY IR AND XRD.

Sample	IR Identifications	XRD Identifications
I Municipal refuse fly ash -	$CaSO_4$	$CaSO_4$
	$ZnSO_4$	-
	Na_2SO_4	-
	K_2SO_4	-
	$KAl(SO_4)_2$	$KAl(SO_4)_2$
	-	$PbSO_4$
	-	NaCl
	-	K_2ZnCl_4
	SiO_2	SiO_2
	Fe_3O_4	Fe_3O_4
	Al_2O_3	-
	Inorganic unknown	Inorganic unknown
	Aliphatic hydrocarbon	-
	Aromatic or olefinic hydrocarbon	-
	Ester carbonyl	-
	Acid carbonyl	
II Municipal refuse fly ash -	$CaSO_4$	$CaSO_4$
	K_2SO_4	-
	$ZnSO_4$	-
	Na_2SO_4	-
	$PbSO_4$	-
	-	NaCl
	-	K_2ZnCl_4
	SiO_2	SiO_2
	Fe_3O_4	Fe_3O_4

TABLE 7. (Continued)

	Sample	IR Identifications	XRD Identifications
II	Municipal refuse fly ash - continued.	Al_2O_3	-
		-	$CaCO_3$
		$XHCO_3$	-
		Inorganic unknown	Inorganic unknown
		Aliphatic hydrocarbon	-
		Aromatic or olefinic hydrocarbon	-
		Ester carbonyl	-
		Acid carbonyl	
		-	Organic unknown
IV	Sewage sludge fly ash -	$(NH_4)_2SO_4$	-
		$CaSO_4$	$CaSO_4$
		$ZnSO_4$	-
		K_2SO_4	-
		Na_2SO_4	-
		$KAl(SO_4)_2$	-
		SiO_2	SiO_2
		Fe_2O_3	-
		$CaHPO_4$, $CaPO_4$, CaP_2O_7	-
		Inorganic unknown	Inorganic unknown
		Aliphatic hydrocarbon	-
		Aromatic hydrocarbon	-
		Aromatic ester	-
		Carboxylic acid	-
		Lactone, anhydride, or peroxide	-
		-	Organic unknown

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